

Supporting information for

**Synthesis, structures and properties of Nickel(II) and Cobalt(II)
metal-organic frameworks based on a flexible tricarboxylate ligand TTG and
different pyridyl-containing ligands**

Su-Na Wang^[a], Yi-Zhi Li^[a], Junfeng Bai^{*[a]}, Yi Pan^[a], Manfred Scheer^[b], Xiao-Zeng You^[a]

[a] State Key Laboratory of Coordination Chemistry, School of Chemistry and Chemical
Engineering, Nanjing University, Nanjing, 210093, P. R. China

E-mail: bjunfeng@nju.edu.cn

^[b] Institut für Anorganische Chemie der Universität Regensburg, 93040 Regensburg

Table S1. Selected Bond Lengths (in Å) and Angles (deg) for complexes **1-4**.

Complex 1					
Ni(1)-N(7)	2.149(4)	O(1)-Ni(1)-O(1W)	87.69(5)	O(2W)-Ni(1)-N(7)	92.20(10)
Ni(1)-O(1)	2.031(4)	O(1W)-Ni(1)-O(3W)	91.44(5)	O(3W)-Ni(1)-N(7)	91.35(11)
Ni(1)-O(1W)	2.047(4)	O(2W)-Ni(1)-O(3W)	89.45(10)	O(1)-Ni(1)-N(8A)	89.40(10)
Ni(1)-O(2W)	2.066(4)	O(1)-Ni(1)-O(2W)	91.41(11)	O(2W)-Ni(1)-N(8A)	89.17(9)
Ni(1)-O(3W)	2.084(4)	O(1)-Ni(1)-N(7)	91.45(10)	O(1W)-Ni(1)-N(8A)	90.58(2)
Ni(1)-N(8A)	2.102(4)	O(1W)-Ni(1)-N(7)	88.06(11)	O(3W)-Ni(1)-N(8A)	87.80(3)
C(5)-O(1)	1.245(7)	C(7)-O(3)	1.287(7)	C(9)-O(5)	1.202(8)
C(5)-O(2)	1.285(7)	C(7)-O(4)	1.209(7)	C(9)-O(6)	1.251(7)
Complex 2					
N(7)-Ni(1)	2.103(3)	O(4B)-Ni(1)-O(1)	174.93(11)	O(4B)-Ni(1)-O(3C)	97.84(10)
N(8)-Ni(1A)	2.100(3)	O(1)-Ni(1)-O(3C)	87.15(10)	O(4B)-Ni(1)-N(8D)	87.13(11)
Ni(1)-O(1)	2.037(2)	O(1)-Ni(1)-N(8D)	87.99(11)	O(3C)-Ni(1)-N(8D)	172.21(11)
Ni(1)-N(8D)	2.100(3)	O(4B)-Ni(1)-N(7)	89.49(11)	O(1)-Ni(1)-N(7)	91.79(11)
Ni(1)-O(4B)	2.013(2)	O(3C)-Ni(1)-N(7)	85.09(11)	N(8D)-Ni(1)-N(7)	88.97(12)
Ni(1)-O(3C)	2.067(2)	O(4B)-Ni(1)-O(1W)	87.74(8)	O(1)-Ni(1)-O(1W)	91.36(8)
Ni(1)-O(1W)	2.1384(19)	O(3C)-Ni(1)-O(1W)	90.84(9)	N(8D)-Ni(1)-O(1W)	95.37(11)
C(5)-O(1)	1.260(4)	C(7)-O(3)	1.252(4)	C(9)-O(5)	1.231(4)
C(5)-O(2)	1.234(4)	C(7)-O(4)	1.247(4)	C(9)-O(6)	1.260(4)
		N(7)-Ni(1)-O(1W)	174.72(12)		
Complex 3					
Co(1)-O(1)	2.060(3)	O(4A)-Co(1)-O(1)	173.19(11)	O(4A)-Co(1)-O(3B)	98.50(10)
Co(1)-N(7)	2.159(3)	O(1)-Co(1)-O(3B)	87.94(11)	O(4A)-Co(1)-N(7)	86.74(11)
Co(1)-O(1W)	2.194(2)	O(1)-Co(1)-N(7)	87.09(12)	O(3B)-Co(1)-N(7)	171.96(12)
Co(1)-O(4A)	2.037(2)	O(4A)-Co(1)-N(8C)	88.96(11)	O(1)-Co(1)-N(8C)	93.76(11)
Co(1)-O(3B)	2.092(2)	O(3B)-Co(1)-N(8C)	85.46(11)	N(7)-Co(1)-N(8C)	88.56(13)
Co(1)-N(8C)	2.170(3)	O(4A)-Co(1)-O(1W)	87.73(8)	O(1)-Co(1)-O(1W)	89.99(9)
C(5)-O(1)	1.248(5)	O(3B)-Co(1)-O(1W)	90.97(9)	N(7)-Co(1)-O(1W)	95.35(12)
C(5)-O(2)	1.261(5)	N(8C)-Co(1)-O(1W)	174.72(12)		
C(7)-O(3)	1.240(4)	C(9)-O(5)	1.245(5)		
C(5)-O(4)	1.256(4)	C(9)-O(6)	1.236(5)		
Complex 4					
Co(1)-O(4A)	2.096(3)	O(4A)-Co(1)-O(1C)	90.86(10)	O(1C)-Co(1)-N(8E)	89.26(11)
Co(1)-O(1C)	2.100(2)	O(4A)-Co(1)-O(1D)	89.14(10)	N(8)-Co(1)-N(8E)	180.00(11)
Co(1)-N(8)	2.161(3)	O(1C)-Co(1)-O(1D)	180.00(13)	O(3F)-Co(2)-O(6G)	102.51(11)
Co(1)-O(4B)	2.096(3)	O(4B)-Co(1)-N(8)	87.39(10)	O(6G)-Co(2)-O(2)	105.45(11)
Co(1)-O(1D)	2.100(2)	O(1D)-Co(1)-N(8)	89.26(11)	O(6G)-Co(2)-N(7)	95.54(12)
Co(1)-N(8E)	2.161(3)	O(4B)-Co(1)-N(8E)	92.61(10)	O(3F)-Co(2)-O(1)	88.89(10)
Co(2)-O(3F)	1.962(3)	O(1D)-Co(1)-N(8E)	90.74(11)	O(2)-Co(2)-O(1)	58.93(9)
Co(2)-O(2)	2.034(2)	O(4A)-Co(1)-O(4B)	180.0	O(3F)-Co(2)-O(2)	138.71(11)
Co(2)-O(1)	2.336(3)	O(4B)-Co(1)-O(1C)	89.14(10)	O(3F)-Co(2)-N(7)	103.01(13)
Co(2)-O(6G)	1.979(3)	O(4B)-Co(1)-O(1D)	90.86(10)	O(2)-Co(2)-N(7)	103.85(12)
Co(2)-N(7)	2.068(3)	O(4A)-Co(1)-N(8)	92.61(10)	O(6G)-Co(2)-O(1)	163.67(11)
		O(1C)-Co(1)-N(8)	90.74(11)	N(7)-Co(2)-O(1)	93.17(11)

Symmetry codes: Complex 1, A: x, y, z+1. Complex 2, A: x, -y, z-1/2; B: x, y-1, z; C: -x+1/2, -y+1, z; D: x, -y, z+1/2; E: x, y+1, z; F: -x+1/2, -y, z. Complex 3, A: x, y+1, z; B: -x+3/2, -y+1, z; C: x, -y+2, z-1/2; D: x, -y+2, z+1/2; E: x, y-1, z; F: -x+3/2, -y+2, z. Complex 4, A: x+1/2, -y+3/2, z-1/2; B: -x+3/2, y-1/2, -z-1/2; C: x, y, z-1; D: -x+2, -y+1, -z; E: -x+2, -y+1, -z-1; F: -x+3/2, y-1/2, -z+1/2; G: -x+1/2, y-1/2, -z+1/2; H: x, y, z+1; I: -x+3/2, y+1/2, -z+1/2; J: -x+3/2, y+1/2, -z-1/2; K: -x+1/2, y+1/2, -z+1/2.

Table S2. Hydrogen bonding geometry in complex **1-3** (in Å and deg).

Complex 1					
D-H...A	<DHA	d(D...A)	D-H...A	<DHA	d(D...A)
N(4)-H(4C)...O(8W)	152.3	2.886(1)	O(8W)-H(8WC)...O(3) ^a	128.4	2.860(1)
O(1W)-H(1WC)...O(7W)	138.0	2.735(5)	O(2W)-H(2WC)...O(6) ^b	144.7	2.713(5)
O(2W)-H(2WB)...O(2)	145.1	2.632(4)	O(3)-H(3)...N(3) ^c	157.7	2.650(5)
O(5W)-H(5WD)...O(7W)	127.6	2.947(3)	O(2W)-H(2WC)...O(5W) ^c	130.6	3.207(4)
O(6W)-H(6WB)...O(5)	177.7	2.788(1)	O(3W)-H(3WB)...O(5W) ^c	129.7	2.728(5)
O(6W)-H(6WC)...O(7W)	124.9	2.857(3)	O(8W)-H(8WD)...O(6) ^d	150.0	3.076(1)
O(7W)-H(7WB)...O(6W)	143.9	2.857(3)	O(3W)-H(3WC)...O(8W) ^e	145.8	2.691(1)
N(6)-H(6C)...O(4) ^a	171.5	2.813(6)	O(4W)-H(4WB)...N(2) ^f	169.5	2.808(4)
Complex 2					
O(1W)-H(1WA)...O(2)	150.2	2.612(3)	N(6)-H(6C)...O(5) ^d	139.5	2.852(4)
O(4W)-H(4WD)...O(2)	178.2	2.813(3)	O(5)-H(5B)...N(2) ^d	140.6	2.648(4)
N(5)-H(5A)...O(3W) ^a	145.8	2.725(4)	O(3W)-H(3WA)...O(6) ^e	162.2	2.586(3)
O(2W)-H(2WB)...O(3) ^b	150.9	2.990(3)	O(3W)-H(3WB)...O(2W) ^f	148.5	3.155(4)
N(4)-H(4C)...O(6) ^c	151.8	3.056(4)			
Complex 3					
O(4W)-H(4WD)...O(2)	178.4	2.795(4)	N(6)-H(6C)...O(5) ^c	141.2	2.874(4)
O(3W)-H(3WB)...O(3) ^a	129.8	3.036(4)	N(5)-H(5D)...O(2W) ^d	145.7	2.943(4)
O(3W)-H(3WC)...O(2W) ^b	126.5	2.896(4)	O(2W)-H(2WC)...O(6)	120.2	2.648(4)
O(3W)-H(3WB)...N(8) ^b	154.4	3.367(4)	N(4)-H(4C)...O(6) ^e	150.4	3.059(5)
O(5)-H(5A)...N(3) ^c	141.9	2.658(4)			

Symmetry codes: Complex **1**, ^ax+1, y, z; ^bx-1, y, z-1; ^cx-1, y, z; ^dx, y, z-1; ^e-x+1, y-1/2, -z; ^f-x+1, y-1/2, -z+1. Complex **2**, ^ax, y, z-1; ^bx, -y+1, z+1/2; ^c-x, y, -z+1/2; ^d-x, -y+1, -z; ^e-x, -y+1, -z+1; ^f-x+1/2, y+1, z+1/2. Complex **3**, ^ax, -y+1, z+1/2; ^b-x+3/2, -y+2, z; ^c-x+2, -y+1, -z; ^dx, -y+1, z-1/2; ^e-x+2, y, -z+1/2.

Table S3. Structural diversity of the eight complexes based on H₃TTG ligand.

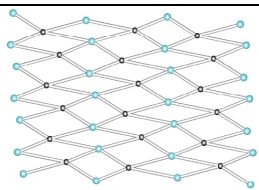
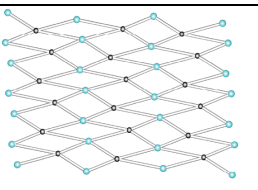
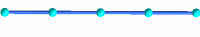
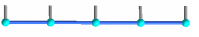
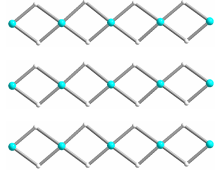
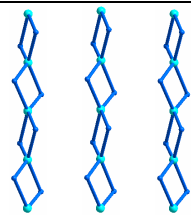
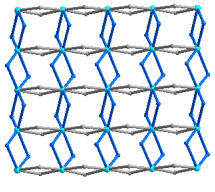
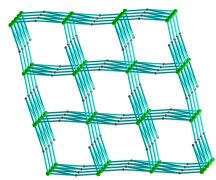
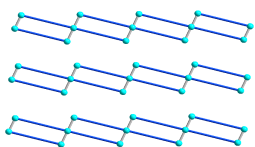
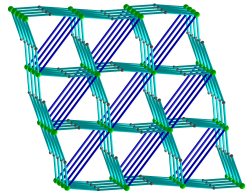
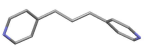
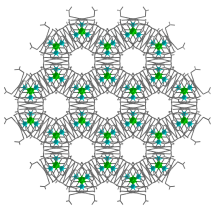
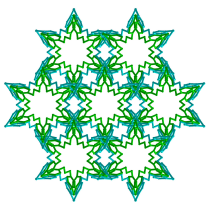
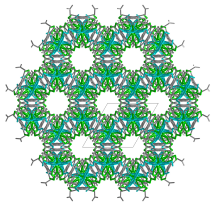
Complex	Base	Metal-acid	Metal-base	Resulting network
[M(HTTG)(H ₂ O) ₂] _n (M=Ni, Co)	No base		No base	
1				
2 and 3				
4				
5 and 6				

Figure S1. Stacking modes of complex **1** along the *c* axis.

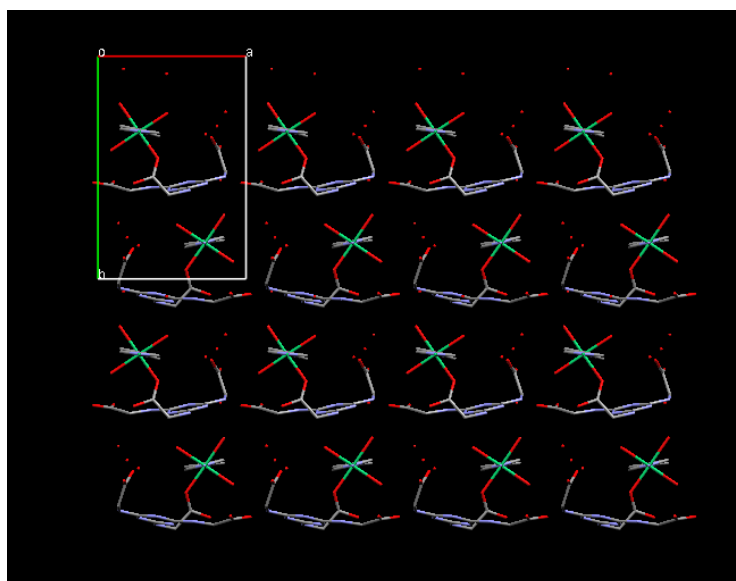


Figure S2. (a) (b) Connectivity of the metal centers with the TTG ligands in complex **4** viewed down *a* and *c* axis, respectively. (c) (d) The whole structure of complex **4** viewed down *a* and *c* axis, respectively. Hydrogen atoms and guest molecules are omitted for clarity.

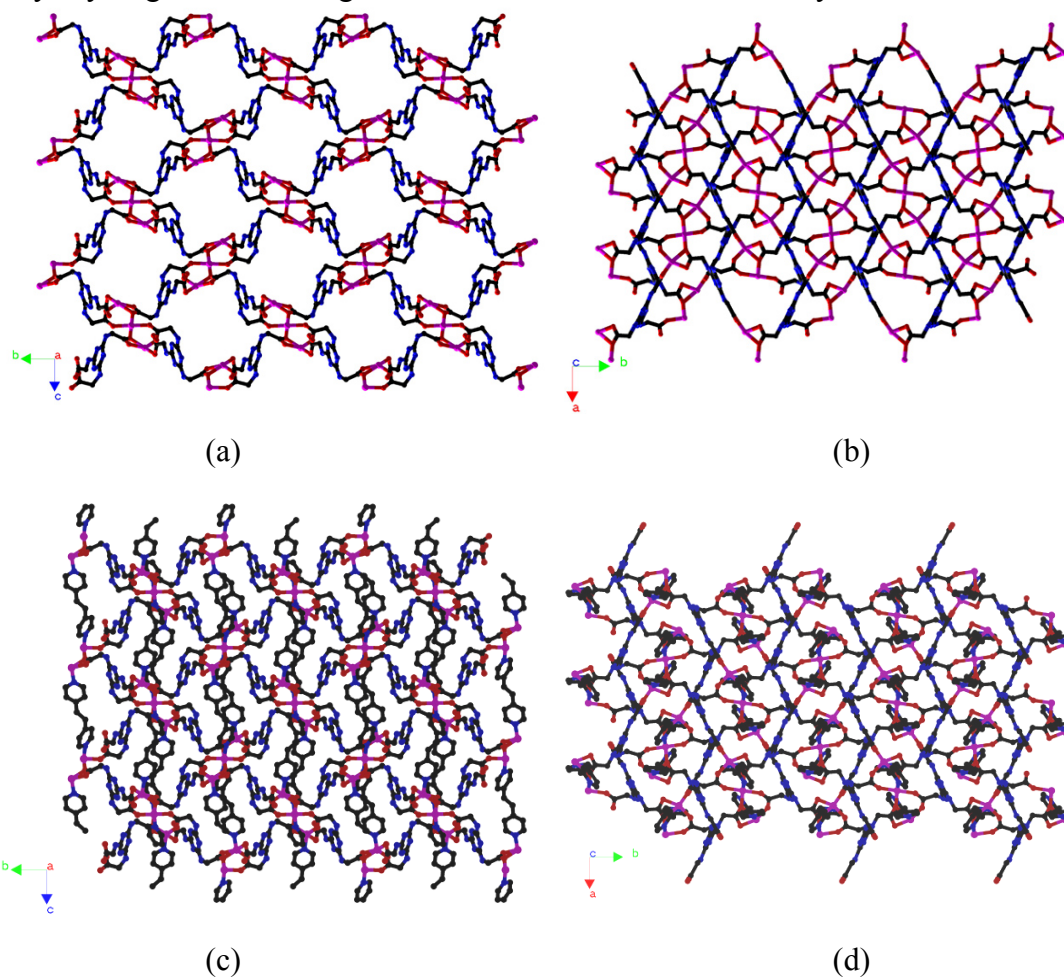


Figure S3. TGA of complex **2** and **3**.

